Ohio Shale (Devonian), SDO-1 from Rowan County, Kentucky

by

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## Abstract

A part of the Huron Member of the Ohio Shale of Late Devonian age from western Rowan County, Kentucky, was selected and prepared as reference sample, SDO-1, to assist in the determination of local and regional variations of the chemical and mineralogic components of the several Devonian-age black shales in the Appalachian basin. The stratigraphy of the sample is discussed and the mineralogy of the sample obtained from thin section examination is given. The sparse published and unpublished data on the sample are listed in several tables and a small experimental design for future analytical work is suggested so that reliable estimates of the chemical composition may be obtained.

## Introduction

The U.S. Geological Survey was involved from 1976 to 1981 with several dozen other cooperating agencies and investigators in an extensive regional study to determine and to document the geologic, geochemical, and geophysical characteristics of the dark gas-producing shales in the Devonian rocks of the Appalachian basin for the U.S. Department of Energy's Morgantown Energy Technology Center (Contract DE-A121-79MC10866). The study was part of an effort to enhance the extraction and recovery of gas from a non-conventional source of natural gas.

We soon realized that a reference sample for the Devonian gas shales was essential to the study, not only to determine local and regional variations of the chemical and mineralogical components of the several black shales in the Appalachian basin, but also for comparison with other black shales worldwide. Consequently we selected for preparation as a reference sample a segment of the Huron Member of the Ohio Shale whose stratigraphy and environment of deposition were well documented. The sample, a black Devonian shale, is a typical example of the so-called "eastern oil shale", in contrast to the oil shale from the Green River Formation of Colorado and adjacent states.

### Stratigraphy

A brownish-black (5YR2/1) shale was obtained by front-end loader, back hoe, and jackhammer from a cut in the Ohio Shale of Late Devonian age along Interstate Highway 64 about 8.5 miles (13.7 km) west of Morehead in western Rowan County, Kentucky, by R.C. Kepferle of the U.S. Geological Survey and William Pfalzer and Brian Gilpin of the Kentucky Department of Transportation on March 14, 1977. The sampled locality, lat 38°09'56"N, long 83°35'38"W (fig. 1), is on the south side of Interstate I-64, 1.6 miles (2.6 km) east of the bridge across the Licking River in the southwest quarter of the Farmers 7 1/2-minute quadrangle (topographic). The base of the exposure is at an elevation of about 690 feet. The locality is accessible and likely will be exposed during the useful life of the Interstate Highway.

The sample, designated SDO-1 for Shale, Devonian, Ohio, was taken from a 10-foot (3.05 m) zone in the lower part of the Huron Member of the Ohio Shale (Pepper, de Witt, and Demarest, 1954, p. 15), which is equivalent to part of the Gassaway Member of the Chattanooga Shale (Hass, 1956, p. 20-23), and to the Dunkirk Shale Member of the Perrysburg Formation of New York (Wallace, Roen, and de Witt, 1977).

Sample SDO-1 was selected as representative of the relatively more radioactive brownish-black to black shale in the Upper and Middle Devonian rocks in the Appalachian basin. Based on a radioactivity profile, the sampled interval was chosen (fig. 2) to include beds that showed high radioactivity as well as a uniform brownish-black (5YR2/1) color. The beds sampled occupy the basal 10 feet (3.05 m) of a uniform 20.3 foot (6.1 m) zone of brownish-black (5YR2/1) shale which was described (Provo, Kepferle, and Potter, 1977, and 1978, Table 1, unit 5) as ".... fissile, brittle, pyritic; weathers blocky and massive in lower two thirds; less resistant in upper one-third of unit; fossils include Tasmanites, conodonts, and woody plant fragments." This unit is overlain by an 8.3-foot (2.53 m) sequence of interpedded greenish-gray (5GY4/1), light-olive-gray (5Y6/1), and olive-black (5Y2/1) shale in which remains of the fossil alga, Foerstia, are abundant (Provo, Kepferle, and Potter, 1978, Table 1, unit 6). The Foerstia zone is a biostratigraphic marker zone, which has been recognized from western New York to southern Tennessee (Murphy, 1973, p. 3406-3407; Schopf and Schwietering, 1970, p. H8) and apparently occupies a short stratigraphic interval throghout this area.

Hand-specimen examination shows that pyrite is abundant as scattered knots, euhedral crystals, nodules, and layers as much as 0.1 foot (3 cm) thick. Vitrinite from coalified plant remains is sparse. Traces of selenite (gypsum) visible on some of the parting planes during sampling were likely the product of near-surface weathering of some of the pyrite.

Thin-section examination shows that the rock is an organic-rich silt shale. The components, in percent in order of abundance, are organic plant (?) maceral, 49; clay (0.002 mm or less), 17; quartz, 15; pyrite, 12; organic sporomorphs, 2.5; gypsum, 2.0; mica, 1.5; feldspar, 0.5; and dolomite, 0.5. The finely shredded organic maceral is identified mainly by a reddish-brown translucent character and may include clay which has been stained by contact with the organic material. The organic shreds are commonly 0.002 mm by 0.006 mm. Sporomorphs are commonly called Tasmanites and occur as flattened translucent pale-yellow to bright-orange bodies 0.006 mm thick and 0.12 mm long. quartz silt as scattered grains or as discrete laminae 1 to 3 grains thick measure 0.038 to 0.058 mm in longest diameter for eight of the coarsest grains. One feldspar grain measured 0.077 mm in longest diameter, but showed signs of overgrowth (untwinned); rare plagioclase feldspar was identified by twinning. Pyrite spheres and euhedral crystals occur singly, 0.005 to 0.01 mm in diameter, as spore fill as much as 0.03 mm in diameter, or as aggregates. Muscovite mica is in frayed flakes which are somewhat distorted by compaction and which are as much as 0.07 mm in diameter. Dolomite and gypsum occur as scattered subhedral crystals or with quartz in the discrete laminae; their maximum diameter is 0.029 mm. Traces of shattered conodonts were found associated with one of the silt laminae.

Compactional features seen in thin section include the draping of organic maceral, clay, and mica flakes around pyrite crystals and silt grains. Flattened Tasmanites are also indicative of compaction. No orientation fabric or alignment of grains could be detected in a thin section cut parallel to the bedding plane of the shale.

# Sample Preparation and Analytical Data

The sample was processed by a variation of the usual procedure (Flanagan, 1967) for preparing reference samples of silicate rocks. The variation was approximately the same as that used for the Green River Shale sample, SGR-1. Discussions at meetings at the Morgantown Energy Technology Center indicated a need for both coarsely ground and powdered samples where the powders would serve for the anticipated types of inorganic analysis. The coarse fraction was prepared for the analysis of organic constituents, as well as for hand and microscopic examination, but was not intended for determinations of inorganic constituents.

The entire bulk sample was passed through a jaw crusher whose plates were set so that the distance between their bottom edges was approximately 3/16-inch (4.7 mm). In addition to yielding coarse material for which the smallest dimension of some coarse pieces frequently exceed a nominal 3/16-inch size, the crushing resulted in a large fraction of fine material, including powder, which is normally obtained in a crushing operation.

The product from the jaw crusher was then passed through a roller crusher with the distance between the rolls set at about 1/8 inch. The product from the roller crusher was thoroughly mixed and about one third of the homogenized material was sampled into 4-ounce (120 mL) amber glass bottles. Occassionally, pieces of shale as large as about 3/16 inch (4.7 mm) may occur in the bottles of the coarse sample.

The remaining two thirds of the crushed sample was passed through the roller crusher a second time with the rolls adjusted so that they just touched to yield a finer-grained product. Batches of about 135 lb (~60 kg) were ground in a ball mill until about 95 percent of the powder in any batch passed a 200-mesh (0.074 mm) screen. All batches of either the coarse or the powdered sample were thoroughly mixed to homogenize the material before either sample was bottled. No attempt was made to fill a bottle to a specified weight of either sample; the bottles were generally not filled to capacity so that they could be rolled to serve as a preliminary mixing before sampling for analysis.

Bottles of either the coarse or the powdered sample, or both, were then sent to those analysts requesting them. Several types of analyses were then begun in the Reston laboratories of the U.S. Geological Survey. Computerized semiquantitative emission spectrographic estimates of elements in the sample (Table 1) were completed by J.L. Harris in April, 1978, as were chemical analysis for the major and minor oxides (Table 2) by N.G. Skinner and F.W. Brown using the methods of Shapiro (1975). Instrumental neutron activation determinations of several elements (Table 3) by the method of Baedecker and others (1977) were completed by L.J. Schwarz in July, 1978. These contributions from the Reston laboratories were held in a special file, pending receipt of data from the analysts to whom the samples were sent.

Skinner and Brown did not determine FeO as part of the chemical analysis because the considerable amount of pyrite in the sample would interfere with the determination of ferrous iron. Similarly, the  $\rm H_2O^+$  content was not determined because some hydrogen in the organic matter of the shale might be converted to  $\rm H_2O$  during the analytical procedure, thereby causing doubt about the validity of the determination of  $\rm H_2O^+$ .

The semiquantitative spectrographic estimates are generally considered as good approximations of the trace element contents of a sample and often suggest minor changes in later chemical procedures so that the best trace element data will be obtained. These estimates are also useful as a preliminary test of the homogeneity of a sample, as the analysis of variance includes the F ratios shown in Table 1. The F ratio allows us to determine if the variation of an element among bottles is significantly greater than the variation within the bottles.

Although a number of sets of samples were sent to the analysts requesting them, no data have been returned to us. Further, the number of data that have been published is sparse, or almost non-existent, considering the effort involved in the collection and preparation of the sample.

Among the few data published were those by Leventhal and others (1978) who listed determinations made by several techniques in the Denver laboratories of the U.S. Geological Survey. Lechler and Leininger (1978) published determinations of 10 major and minor oxides in samples SDO-1 and SIND-1 (Shale, Indiana, Devonian -1), the latter apparently a black Devonian shale prepared by the Indiana Geological Survey. The determinations were by inductively coupled argon plasma (ICAP), colorimetric, atomic absorption, and atomic emission methods for data by the Indiana Geological Survey, and data by the Illinois Geological Survey for the same oxides for which the methods were not specified.

Lechler and Leininger (1979) published the same major and minor oxide data but specified methods for four of the oxides determined by the Illinois Geological Survey. They list their data for 11 trace elements by ICAP and include averages of data by other laboratories. The laboratories are not identified, nor are references given. They also include a table of the trace element contents of SIND-1 by both atomic absorption spectrometry (AAS) and ICAP. Lechler and others (1980) list essentially the same data for the major and minor oxides and for trace element contents in a paper on the analysis of 12 soil reference samples from the southeastern United States (Barnhisel, 1978).

Instrumental neutron activation determinations of elements in SDO-1 and SIND-1, as well as in the sample of the Cody Shale, SCo-1 (Schultz and others, 1976), were reported by Frost and others (1982). The average of four determinations of the mercury content of SDO-1 was reported by Flanagan and others (1982) as 95.6 parts per billion (ppb), as compared to 52.3 ppb for seven portions of the Cody Shale sample, SCo-1, and to 274 ppb for seven portions of the Green River Shale SGR-1. Unpublished arsenic data by W.M. d'Angelo, U.S. Geological Survey (written commum, 1984) show that the averages, in parts per million, of four determinations for each of these three shale samples are: SDO-1, 79.8 ppm; SGR-1, 78.5 ppm; and SCo-1, 17.2 ppm.

The published and unpublished data mentioned for SDO-1 are collected in Table 4. Because of the scarcity of data in Table 4, there appears to be no compelling reason for a discussion of the geochemistry of SDO-1 versus that of the other shales, SGR-1 and SCo-1. However, included among the six portions of SDO-1 for which data are reported in Table 3 were six portions of SGR-1 using the same experimental design, and these 12 portions of sample were included in the same irradiation. The averages for the two samples are given in Table 5 where data for Ba, Rb, La, Yb, and Lu in SGR-1 are footnoted to indicate that these data are the averages of five determinations because the counts for portion 1, bottle 1 of the sample were lost during data processing.

Included in Table 5 with our data for SDO-1 and SGR-1 are estimates by Gladney and Goode (1981) for the shales, SGR-1 and SCO-1. Our INAA data for SDO-1 and SGR-1 offer a comparison of the trace element contents of these samples where the data were obtained under the same conditions, whereas a comparison with the data for SGR-1 in the compilation by Gladney and Goode (1981) for SCO-1 are entered to show differences in the trace element contents among the three shales.

One striking feature of the data is the high uranium content of SDO-1 that results in a Th/U ratio of about 0.2, roughly the inverse of the ratio that one sees for igneous rocks. The ratios increase from SDO-1 (0.2) through SGR-1 (0.7) to SCO-1 (3), where the ratio for SCO-1 is approaching that usually obtained for igneous rocks.

# Future Analytical Data

The experimental design with three bottles of a sample as shown in Tables 1-3, in which two sample portions from each bottle are randomized as a group before analysis, has been a useful procedure to determine if a constituent of a sample is distributed homegeneously among the bottles. Because there have been so few data published on sample SDO-1, we have reduced the size of the experimental design from three bottles to two while retaining the same number of portions per bottle for analysis as part of an effort to persuade scientists to analyze the sample. Future data obtained with the smaller design may be compared directly with the major and minor oxide data in Table 2 and with the trace element data in Table 3.

We plan to calculate best estimates of the contents of any element or oxide by the method described by Flanagan (1984). The estimates may be obtained by the sequential procedure of (1) calculating a homogeneous variance for sets of  $\underline{n}$  determinations for a constituent, (2) calculating from this variance the standard deviation of the means of  $\underline{n}$  determinations, and (3) using this standard deviation to Studentize the range of means to decide which means could have been derived from the same population.

The data in Tables 2 and 3 may be used for the calculations above, even though there are six determinations, whereas the smaller design requires only four. In anticipation of future data for a study on clay reference samples

for which the smaller design is also used, one of us decided to include data for a sample, NBS-98a, plastic clay (Table 3, Flanagan and others, 1977), for which there were three bottles and therefore six determinations. To reduce the number of data to the four required by the smaller design, the random number generator of a hand calculator was used to retain the first two of the bottle numbers, 1, 2, and 3, that appeared in the units place of two-digit random numbers obtained consecutively. This resulted in retaining data for bottles 1 and 3, and discarding data for bottle 2 for the new clay study. The identical procedure will be used for data for bottles 1, 2, and 3 in Tables 2 and 3 of this paper.

The only strict requirement for the calculations of best estimates is that the means and variances of data must be calculated from the same number of determinations by each analyst. Determinations may be made on four portions from the same bottle. The use of the smaller design, however, has the advantage that the data may first be used to detect sources of heterogeneity, if any, and the same data may then be used to calcualte best estimates.

The finely ground SDO-1 will be available at two bottles per box for those analysts who wish to use the experimental design.

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Table 1. Computerized semiquantitative spectrographic determinations of trace elements in SDO-1 by J.L. Harris, USGS, and estimates from the analysis of variance

[In parts per million. df degrees of freedom. NS, not significant. Neg., a negative bottle variance was obtained in the analysis of variance. F ratios tested against  $F_{0.95}(2,3) = 9.55$ , or the fractile indicated.]

				Standard Deviation			
		Bottle			Bottle	Error	F
	1	2	3	Mean	<u>df 2</u>	<u>df 3</u>	<u>ratio</u>
В	190	150	170	170	Neg.	15.3	0.64 NS
	170	180	160				
Ва	340	340	410	<b>3</b> 60	Neg.	28	.85 NS
	350	370	350				
Ве	5.5	6.3	5.4	5.7	.73	.33	10.68 NS (.975)
<b>C</b> .	5.0	6.8	5.0	00			
Се	68	86	84	80	8.4	5.6	5.48 NS
<b>C</b> .	60 20	97	86	26.5.			1.51.10
Со	38	32	39	36.5 ·	1.4	2.6	1.54 NS
C-	34	37 47	39	<b>F</b> .C	0.0	7.0	1 10 15
Cr	59	47	69	56	2.2	7.2	1.19 NS
C	52 76	55 76	55 76	75 6	0.7	71	4 00 10
Cu	76	76	75 74	75.5	.87	.71	4.00 NS
Ga	75 18	77 16	74 21	10 5	Noa	1.0	. C2 NC
ua	19	19	18	18.5	Neg.	1.8	.63 NS
Gd	13	11	12	11.5	Neg.	1.2	.33 NS
uu	10	11	12	11.5	neg.	1.2	.33 N3
La	35	39	38	37.8	4.6	4.2	3.40 NS
La	28	42	35	37.0	4.0	4.2	3.40 113
Mn	480	450	520	443	Neg.	<b>6</b> 8	.46 NS
	340	440	430	773	neg.	00	•40 113
Мо	110	100	120	109	8.0	7.7	3.14 NS
	94	110	120	103	0.0	, , ,	0114 110
Nb	8.6	9.6	9.5	9.5	1.4	1.5	2.84 NS
	6.4	11	12				
Ni	94	76	99	89	6.4	7.0	2.68 NS
	82	88	97				
Pb	36	30	37	34.7	1.2	2.2	1.63 NS
	34	35	35				
Sc	12	14	12	12.6	1.4	1.3	3.29 NS
	9.6	14	14				
Sr	110	. 96	110	106	Neg.	7.0	.53 NS
	100	110	110				
٧	140	130	120	133	6.4	5.8	3.50 NS
	140	140	130				
Y	29	<b>3</b> 3	28	31	3.1	5.5	1.63 NS
	- 22	36	39				
Yb	5.1	4.7	4.9	5.0	Neg.	•57	.80 NS
	5.2	6.0	4.4				
Zn	64	63	74	65	2.8	3.9	2.03 NS
_	61	63	65			•	
Zr	98	130	95	112	Neg.	27	.52 NS
	79	130	140				

Table 2. Determinations of major and minor oxides in SDO-1 by N.G. Skinner and F.W. Brown, USGS

[In percent. df, degrees of freedom. NS, not significant. Neg., a negative bottle variance was obtained in the analysis of variance. Fe  $_20_3$ T, total Fe as Fe  $_20_3$ . F ratio tested against F $_{0.95}(2,3)$  = 9.55. Method: Shapiro (1975).]

						Standard Deviation	
	<del>- 1</del>	2	3	Mean	Bottle df 2	Error df 3	F ratio
	******					<del></del>	
SiO <sub>2</sub>	49.90 50.17	50.10 50.17	50.07 49.90	50.05	Neg.	0.13	0.66 NS
Al <sub>2</sub> 0 <sub>3</sub>	13.23 13.23	13.13 13.13	13.13 12.84	13.12	.09	.12	2.15 NS
Fe <sub>2</sub> 0 <sub>3</sub> T	9.45 9.18	9.43 9.36	9.14 9.48	9.34	Neg.	.18	.14 NS
Mg0	1.57 1.55	1.56 1.55	1.56 1.53	1.55	Neg.	•02	.43 NS
Ca0	1.09 1.07	1.07 1.08	1.07 1.00	1.06	.01	.03	1.29 NS
Na <sub>2</sub> 0	.44 .39	.44 .38	.37 .36	.40	.02	.03	1.50 NS
K <sub>2</sub> 0	3.29 3.44	3.37 3.40	3.45 3.39	3.39	Neg.	•07	.23 NS
TiO <sub>2</sub>	.73 .73	.73 .73	.73 .73	.73	0	0	-
P <sub>2</sub> 0 <sub>5</sub>	.12 .14	.14 .15	.13 .14	.14	0	.01	1.00 NS
Mn0	.03 .04	.04 .04	.04 .04	.04	Ne g∙	.004	.94 NS
CO <sub>2</sub>	1.26 1.06	.97 .97	1.11 1.06	1.07	.07	.08	2.59 NS
LOIa	18.36 18.55	18.56 18.56	18.43 18.51	18.50	Neg.	.08	.91 NS

aLoss on ignition, less CO<sub>2</sub>.

Table 3. Instrumental neutron activation determinations of elements in SDO-1 by L.J. Schwarz, USGS

[In parts per million, except Fe and Na in percent. df, degrees of freedom. NS, not significant. Neg., a negative bottle variance was obtained in the analysis of variance. F ratios tested against  $F_{0.95}(2,3) = 9.55$ . Ratios for Gd and Tm tested against  $F_{0.95}(1,2) = 18.5$ . Method: Baedecker and others (1977).]

Fe					Standard Deviation					
Fe 5.86 5.92 6.59 6.39 Neg. 0.54 <1 NS 6.74 6.73 6.52 2.24 .28 .27 .03 .02 1.29 NS .29 .27 .30 .88 .513 559 616 633.3 Neg. 1.8 <1 NS 778 661 673			Bottle			Bottle	Error	F		
Na       2.74       6.73       6.52       2.24       2.30       .27       .03       .02       1.29       NS         Ba       513       559       616       633.3       Neg.       .18       <1       NS         778       661       673       Neg.       3.4       <1       NS         45.7       46.0       44.6       45.1       43.53       Neg.       3.4       <1       NS         45.7       46.0       44.6       6.9       61.9       59.62       Neg.       3.8       <1       NS         6.2       6.2       6.0       Heg.       .49       <1       NS         6.2       6.2       6.0       Heg.       .49       <1       NS         6.2       6.2       6.0       Heg.       .49       <1       NS         6.2       6.2       6.0       Heg.       .35       <1       NS         Rb       105       113       140       124.7       Neg.       16.8       <1       NS         141       125       124       4.1       Neg.       .51       <1       NS         14       4.6       3.9       4.4		11	2	3	Mean	df 2	df 3	ratio	_	
Na         .25         .24         .28         .27         .30         .20         1.29         NS           Ba         513         559         616         633.3         Neg.         .18         <1	Fe				6.39	Neg.	0.54	<1	NS	
Ba 513 559 616 633.3 Neg. 18 <1 NS 778 661 673 673 Neg. 21 NS 778 661 673 673 Neg. 3.4 <1 NS 45.7 40.1 45.1 43.53 Neg. 3.4 <1 NS 45.7 46.0 44.6 673 Neg. 3.8 <1 NS 65.9 61.9 59.62 Neg. 3.8 <1 NS 65.9 61.9 59.62 Neg. 3.8 <1 NS 65.2 6.2 6.0 Neg. 49 <1 NS 65.2 6.2 6.0 Neg. 35 ×1 NS 65.2 6.2 6.0 Neg. 35 ×1 NS 42.3 4.2 4.2 Neg. 35 ×1 NS 141 125 124 Neg. 16.8 ×1 NS 141 125 124 Neg. 16.8 113 Neg. 16.8 ×1 NS 141 125 124 Neg. 16.8 113 NS 140 124.7 Neg. 16.8 ×1 NS 141 125 124 Neg. 16.8 110 NS 110 114 1.09 Neg. 18 110 1.14 1.09 Neg. 18 Neg. 18 110 1.14 1.09 Neg. 18 Neg. 18 110 1.14 1.09 Neg. 18 Neg. 18 Neg. 18 110 1.00 1.14 1.09 Neg. 18 Neg. 18 Neg. 10.5 10.0 10.2 Neg. 10.5 Neg. 10.5 10.0 10.2 Neg. 10.5 Neg.										
Ba         513         559         616         673         778         661         673           Co         39.7         40.1         45.1         43.53         Neg.         3.4         <1	Na				.27	.03	.02	1.29	NS	
Co 39.7					c22 2		10			
CO         39,7         40,1         45,1         43,53         Neg.         3.4         <1         NS           Cr         54,4         56,9         61,9         59,62         Neg.         3.8         <1	В <b>а</b>				633.3	Neg.	.18	<1	NS	
Cr         54.4         56.9         61.9         59.62         Neg.         3.8         <1         NS           Cs         54.4         56.9         61.9         59.62         Neg.         .49         <1         NS           Cs         5.3         5.6         6.5         6.0         Neg.         .49         <1         NS           Hf         3.7         3.6         4.2         4.0         Neg.         .35         <1         NS           Rb         105         113         140         124.7         Neg.         16.8         <1         NS           Sb         3.5         3.9         4.4         4.1         Neg.         .51         <1         NS           Ta         .88         1.14         .95         .97         Neg.         .18         <1         NS           Ta         .88         1.14         .95         .97         Neg.         .18         <1         NS           Ta         .9.0         8.7         10.5         9.8         Neg.         .82         <1         NS           Lu         41.9         40.9         60.3         50.7         Neg.         .92         <	0-				42.52		2.4			
Cr         54.4         56.9         61.9         59.62         Neg.         3.8         <1         NS           Cs         5.3         5.6         6.5         6.0         Neg.         .49         <1	CO				43.53	мед.	3.4	<1	N5	
Cs 5.3	Cm				E0 62	Nog	2.0	<b>21</b>	NC	
CS         5,3         5,6         6.5         6.0         Neg.         .49         <1         NS           Hf         3.7         3.6         4.2         4.0         Neg.         .35         <1	Cr.				39.02	Ney.	3.0	<b>\1</b>	ИЭ	
Hf       3.7       3.6       4.2       4.0       Neg.       .35       <1       NS         Rb       105       113       140       124.7       Neg.       16.8       <1	C c				6.0	Noa	40	<b>21</b>	MC	
Hf       3.7       3.6       4.2       4.0       Neg.       .35       <1       NS         Rb       105       113       140       124.7       Neg.       16.8       <1	03				0.0	Neg.	•43	`1	143	
Rb       105       113       140       124.7       Neg.       16.8       <1       NS         Sb       3.5       3.9       4.4       4.1       Neg.       .51       <1	Нf				4.0	Neg.	.35	<1	NS	
Rb         105 141         113 125         140 125         124.7         Neg.         16.8         <1         NS           Sb         3.5         3.9         4.4         4.1         Neg.         .51         <1	***					neg.	•••			
141   125   124   125   124   126   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125   124   125	Rh				124.7	Nea.	16.8	<1	NS	
Sb       3.5       3.9       4.4       4.1       Neg.       .51       <1       NS         Ta       .88       1.14       .95       .97       Neg.       .18       <1	TO .				22.00	neg.	10.0	. `-	145	
Ta	Sb				4.1	Nea.	.51	<1	NS	
Ta							,,,	-		
Th	Ta				.97	Nea.	.18	<1	NS	
Th	. •				• • • • • • • • • • • • • • • • • • • •			•		
U 41.9 40.9 60.3 50.7 Neg. 9.2 1 NS 54.5 56.6 50.2  Zn 66 59 66 65.8 Neg. 3.9 1 NS 69 68 67  Zr 310* 332* 270* 318* Neq. 42.3 1 NS 311* 313* 372*  Sc 11.21 11.39 12.65 12.30 Neg96 1 NS 13.07 12.84 12.61  La 30 32 35 33.7 Neg. 2.4 1 NS 35 35 35  Ce 65 69 71 70.8 Neg. 4.6 1 NS 75 74 71  Nd 34 36 40* 39.3 Neg. 4.5 1 NS 8.8 8.9 8.4  Eu 1.31 1.32 1.47 1.43 Neg. 1.1 1 NS 8.8 8.9 8.4  Eu 1.31 1.32 1.47 1.43 Neg. 11 1 1 NS 6d 5.1 (.59)** 6.7 6.15 .95 38 13.5 NS 5 5.8  Th .99 1.05 1.30 1.16 Neg. 1.3 1 NS 1.24 1.19 1.16  Ho 2.3 2.7 1.7 3.3 Neg. 1.5 1 NS 4.1 5.1 3.8  Tm .53 (.42)** .58 .56 Neg. 0.8 1.5 1 NS 1.6548  Lu .46 .45 .54 .50 Neg. 0.05 1.10 NS	Th				9.8	Neg.	.82	<1	NS	
Zn 66 59 66 65.8 Neg. 3.9 1 NS 69 68 67  Zr 310* 332* 270* 318* Neq. 42.3 1 NS 311* 313* 372*  Sc 11.21 11.39 12.65 12.30 Neg96 1 NS 13.07 12.84 12.61  La 30 32 35 35 35  Ce 65 69 71 70.8 Neg. 4.6 1 NS 75 74 71  Nd 34 36 40* 39.3 Neg. 4.5 1 NS 8.8 8.9 8.4 8.8 8.9 8.4  Eu 1.31 1.32 1.47 1.43 Neg11 1.1 NS 1.54 1.49 1.47  Gd 5.1 (.59)** 6.7 6.15 .95 38 13.5 NS 5.8 - 7.0  Tb .99 1.05 1.30 1.16 Neg13 1.5 NS 1.24 1.19 1.16  Ho 2.3 2.7 1.7 3.3 Neg. 1.5 1 NS 1.5						•				
Zn       66       59       66       65.8       Neg.       3.9       <1       NS         69       68       67       310*       332*       270*       318*       Neq.       42.3       <1	U	41.9	40.9	60.3	50.7	Neg.	9.2	<1	NS	
Zr       310* 332* 270* 318* Neq.       42.3       <1 NS		54.5	56.6	50.2		••				
Zr       310*       332*       270*       318*       Neq.       42.3       <1       NS         311*       313*       372*       12.30       Neg.       .96       <1	Zn	66	59	66	65.8	Neg.	3.9	<1	NS	
311*     313*     372*       Sc     11.21     11.39     12.65     12.30     Neg.     .96     <1		69	68	67						
Sc       11.21       11.39       12.65       12.30       Neg.       .96       <1	Zr	310*	332*	270*	318*	Neq.	42.3	<1	NS	
La 30 32 35 35 3.7 Neg. 2.4 <1 NS 35 35 35 35		311*	313*	372*						
La 30 32 35 33.7 Neg. 2.4 <1 NS 35 35 35 35 35 35 35 35 35 35 35 35 35	Sc	11.21	11.39	12.65	12.30	Neg.	.96	<1	NS	
Ce 65 69 71 70.8 Neg. 4.6 <1 NS 75 74 71 70.8 Neg. 4.5 <1 NS 44* 40* 42										
Ce       65       69       71       70.8       Neg.       4.6       <1       NS         75       74       71       39.3       Neg.       4.5       <1	La				33.7	Neg.	2.4	<1	NS	
Nd       75       74       71         Nd       34       36       40*       39.3       Neg.       4.5       <1										
Nd	Ce				70.8	Neg.	4.6	<1	NS	
44*       40*       42         Sm       7.5       7.3       8.9       8.3       Neg.       .87       <1								_		
Sm       7.5       7.3       8.9       8.3       Neg.       .87       <1	Nd				39.3	Neg.	4.5	<1	NS	
Eu 1.31 1.32 1.47 1.43 Neg11 <1 NS 1.54 1.49 1.47	C				0.0	M = -	07	.4	шс	
Eu 1.31 1.32 1.47 1.43 Neg11 <1 NS 1.54 1.49 1.47 6.15 .95 .38 13.5 NS 5.8 - 7.0   Tb .99 1.05 1.30 1.16 Neg13 <1 NS 1.24 1.19 1.16   Ho 2.3 2.7 1.7 3.3 Neg. 1.5 <1 NS 4.1 5.1 3.8   Tm .53 (.42)** .58 .56 Neg08 <1 NS .6548   Yb 3.1 3.1 3.1 3.4 3.3 .05 .20 1.12 NS 1.12 NS 1.14 3.5 3.5 3.3 3.6   Lu .46 .45 .54 .50 Neg05 <1 NS	SM				8.3	Neg.	.87	<1	N2	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	r.,				1 42	Non	11	- 11	мс	
Gd 5.1 (.59)** 6.7 6.15 .95 .38 13.5 NS 5.8 - 7.0  Tb .99 1.05 1.30 1.16 Neg13 <1 NS 1.24 1.19 1.16  Ho 2.3 2.7 1.7 3.3 Neg. 1.5 <1 NS 4.1 5.1 3.8  Tm .53 (.42)** .58 .56 Neg08 <1 NS .6548  Yb 3.1 3.1 3.4 3.33 .05 .20 1.12 NS 3.5 3.3 3.6  Lu .46 .45 .54 .50 Neg05 <1 NS	Eu				1.43	Neg.	•11	<b>\1</b>	ИЭ	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	C4		1.49 / 50\**		6 15	05	20	12.5	мс	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	du				0.15	• 90	• 30	13.3	NO	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Th				1 16	Neg	13	<b>21</b>	MS	
Ho 2.3 2.7 1.7 3.3 Neg. 1.5 <1 NS 4.1 5.1 3.8 Tm .53 (.42)** .58 .56 Neg08 <1 NS .6548 Yb 3.1 3.1 3.4 3.3 .05 .20 1.12 NS 3.5 3.3 3.6 Lu .46 .45 .54 .50 Neg05 <1 NS	ID				1.10	Neg.	•13	<b>\1</b>	NS	
4.1     5.1     3.8       Tm     .53     (.42)**     .58     .56     Neg.     .08     <1	Но				3.3	Nea.	1.5	<1	NS	
Tm	110				0.0	neg.	1.5	`-		
.6548 Yb 3.1 3.1 3.4 3.33 .05 .20 1.12 NS 3.5 3.3 3.6 Lu .46 .45 .54 .50 Neg05 <1 NS	Tm				-56	Nea.	.08	<b>&lt;</b> 1	NS	
Yb 3.1 3.1 3.4 3.33 .05 .20 1.12 NS 3.5 3.3 3.6 Lu .46 .45 .54 .50 Neg05 <1 NS			•		•••		•00	•	.,,5	
3.5 3.3 3.6 Lu .46 .45 .54 .50 Neg05 <1 NS	Yb				3.33	.05	.20	1.12	NS	
Lu .46 .45 .54 .50 Neg05 <1 NS										
	Lu	.46	.45	.54	.50	Neg.	.05	<1	NS	
	*	.53	.53	.48						

<sup>\*</sup> Correction for fission product interference exceeds 20 percent of reported value.

<sup>\*\*</sup> Datum not included in calculations.

Table 4. Summary of data on SDO-1, Devonian Oil Shale, and tentative values

	Sources of data						Tentative		
	(1) <sup>a</sup>	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Values
				In	percent			. —	
\$102	57.3	50.05	-	-	_	49.9	49.9	-	49.9
S10 <sub>2</sub> A1 <sub>2</sub> 0 <sub>3</sub> _	12.6	13.12	-	-	13.1	12.1	12.0	-	12.6
۱Fe₂0ءT	7.0	9.34	9.14	-	9.75	9.65	9.22b	-	9.42
l MgO	1.7	1.55	-	-	1.59	1.47	1.29	-	1.54
Ca O	1.3	1.06		-	1.20 <sup>C</sup>	1.09	1.01	•	1.1
Na <sub>2</sub> O	.33	.40	.37	-	.60 <sup>c</sup>	.42	.38	39	.39
K <sub>2</sub> ð	3.6	3.39	-	-	3.41	3.36	3.29b	3.55	3.40
T102	.41 .17	.73 .14	-	-	1.01 .10 <sup>c</sup>	.69	.74	• ·	.79
P <sub>2</sub> 05 Mn0	.06	.04	-	-	.042	.11	.10	• •	.11 .41
CO <sub>2</sub>	- 00	1.07	_	-	.042	.041	- 043	-	1.07
S	-	-	-	5.56		_	_	_	5.5
ĽOI	-	18.50d	-	-	-	_		-	18.50
				In parts	per milli	on .		•	
As	-	80 <sup>e</sup>	-	104			-	79	80?
В	170	-	-	-	_	-	_		(170)
Ba	360	-	633	_	-	_	-	550	600
Be	6	-	-	-	-	_	-	-	(6)
Br	-	-	-	-	-	-	-	3.6	3.6
Cd		-	÷	-	-	3	-	-	3
Co	37	-	43.5	7	-	-	-	44	44
Cr	56	-	59.6	70 <sup>f</sup>	-	65	-	61	62
Cs	7	-	6.0	-	-		-	-	6
Cu	76	-	-	20 <sup>f</sup>	-	65	-		65
Ga	18.5	-		201	-	-	-	19	19
Hf Hg	-	.0969	4.0	.19	-	-	-	•	4 .15
ng Mn	443	.090	-	.19	-	-	-	332	330
Mo	106	_	-	122	-	156	-	332 157	150
Nb	9.5	_	_	122	-	130	-	13/	(9)
Ni	89	-	-	_	-	100	_	98	100
Pb	35	_	-	20 <sup>f</sup>	-	35	-	-	35
Rb	-	-	124.7	-	_	_	_	127	125
Sb	-	-	4.1	-	-	-	_	-	4
Sc	12.6	-	12.30	15 <sup>f</sup>	-	-	-	15.2	14
Sr	106	-	-	150f	-	76	-	93	85
Ta	-	-	.97	-	-	-	-	. • .	1
Th .:	-	-	9.8		-	9	-	9.5	9.4
U	122	-	50.7	55.6 <sup>f</sup>	-		-	52	52
V Y	133 31	-	-	161 f 50 f	-	1 57 50	-	•	150 50
Zn	65	_	65,8	_	-	70	-	67	68
Zr	112	-	318h	150 <sup>f</sup>	-	, o	-	٠,-	3007
	38			50 <sup>f</sup>				42.0	38
La Ce	38 80	-	33.7 70.8	50'	-	-	-	42.8	38 70
Nd	-	-	39.3	-	-	-	-	•	39
Sm .	-		8.3	-	-	-	-	-	39 8
Eu	2	-	1.43	-	-	_	_	_	1.4
Gď	11.5	_	6.1	-	-	•	-	-	6
Tb		-	1.16	-	-	_	-		1.2
Ho	-	-	3.3	_	-	-	-	-	3.3
Tm	-	-	.53	•	-	-	-	-	.5
Yb	5	-	3.3	3 <sup>F</sup>	-	-	-	2.9	3.1
Lu	-	-	.50	-	-	-	-	-	.5

Sources of data:

b Average of data by X-ray fluorescence and neutron activation.

ources of data:
(1) Unpublished computerized semiquantitative spectrographic estimates by J. L. Harris, USGS (table 2).
(2) Unpublished rapid rock (principally atomic absorption) determinations by N. G. Skinner and F. W. Brown (table 3). Method: Shapiro (1975).
(3) Unpublished instrumental neutron activation determinations by Louis J. Schwarz, USGS (table 4). Method: Baedecker and others (1977).
(4) Leventhal and others (1978).
(5 - 7) Lechler and Leininger (1979). Data of the Indiana Geological Survey by atomic absorption in col. 5 and by inductively coupled plasma spectrometry in col. 6. Data by the Illinois Geological Survey in col. 7.
(8) Frost and others (1982).

<sup>&</sup>lt;sup>a</sup> These and other semiquantitative spectrographic data were not considered for tentative values. They were used as tentative values in parentheses when they were the only data.

By colorimetry.
Loss on ignition less CO<sub>2</sub>.

E Unpublished arsenic data by W. M. D'Angelo, USGS.

Semiquantitative spectrographic estimates.

<sup>9</sup> Flanagan and others (1982) n Corrections for fission product interference exceeded 20 percent of reported values

Table 5. Average trace element contents of three shale samples [In parts per million. n.d., no data or ranges only.]

	SD0-1a	SGR-1a	SGR-1b	SCo-1b
B <b>a</b>	633.3	298.6 <sup>c</sup>	320	580
Co	43.5	11.2	12	10
Cr	59.6	29.4	32	67
Cs	6.0	4.9	5 <b>.</b> 2	7 <b>.</b> 5
Hf	4.0	1.25	1.35	4.26
Rb	124.7	78.6 <sup>c</sup>	85	118
Sb	4.1	3.15	3.3	2.51
Ta	.97	.46	.53	.91
Th	9.8	4.45	4.90	10.1
U	<b>50.</b> 7	6.38	5.57	3.09
Zn	65.8	72.2	80	106
Zr	318d	58.7d	56	160
Sc	12.3	4.8	4.7	10.6
La	33.7	18.8 <sup>c</sup>	n.d.	35
Ce	70.8	32.7	42	62
Nd	39.3d	15.2	14	26
Sm	8.3	2.8	2.7	5.3
Eu	1.43	.43	.60	1.2
Gd	6.2 <sup>e</sup>	2.6	n.d.	5
Tb	1.2	.33	.37	•75
Ho	3.3	<2	<1	.93
Tm	.56e	<.3	.18	.35
Yb	3.3	.94 <sup>c</sup>	1.1	2.6
Lu	.50		.20	.37

a This work.

b Estimates from Gladney and Goode (1981).

<sup>&</sup>lt;sup>C</sup> Average of 5 determinations.

 $<sup>^{\</sup>rm d}$  Some or all determinations were subject to corrections for fission product interference exceeding 20 percent of values.

e Average of 4 determinations.

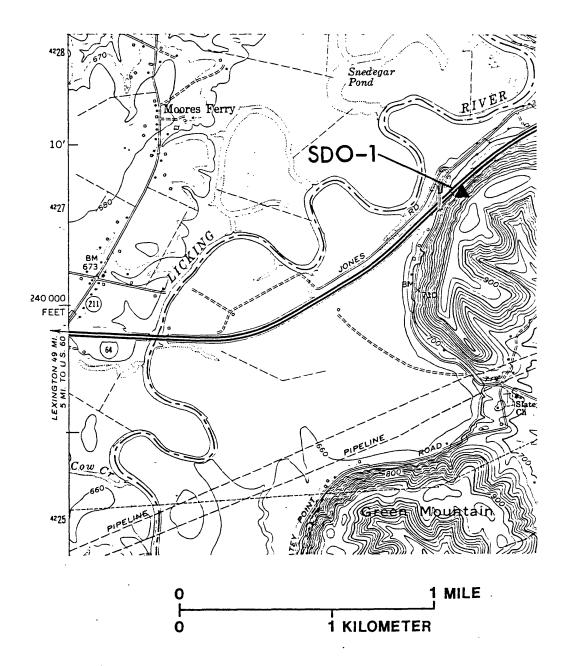


Figure 1. Location of sample SDO-1 on U.S. Highway I-64, Farmers  $7-\frac{1}{2}$  minute quadrangle, Rowan County, Kentucky.

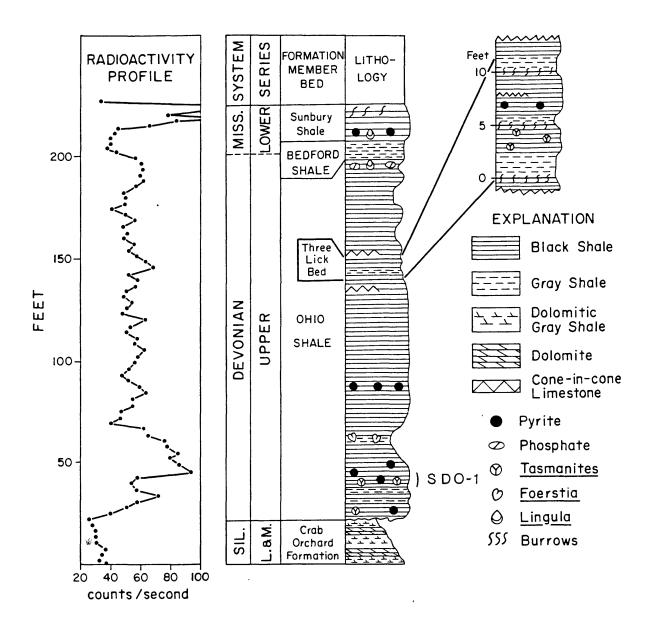


Figure 2. Stratigraphic location of sample SDO-1 and radioactivity profile of the Ohio Shale and associated rocks (adopted from Provo, Kepferle, and Potter, 1978, fig. 2).